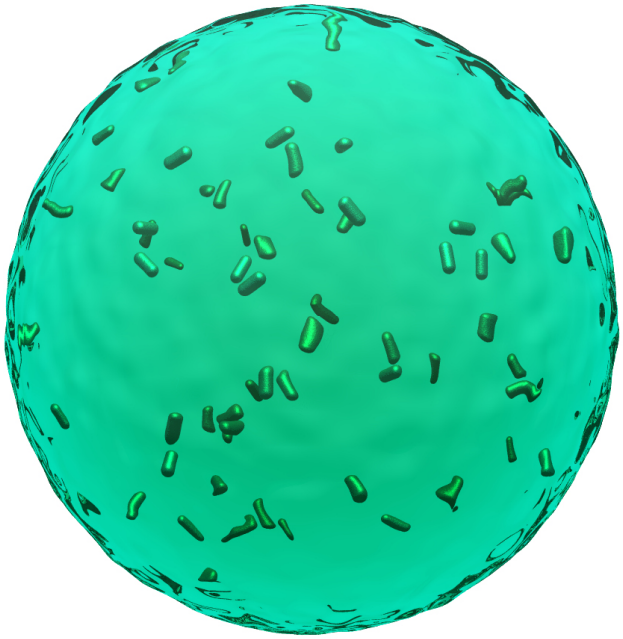

# Development of New Methods for the Synthesis of Plasmonically-Active Precious Metal Rods and Shells

**A thesis presented for the degree of Doctor of Philosophy**

**By**

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**B. Sc. Hons. (Nanotechnology): University of Technology, Sydney**

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## Dedication

This thesis is dedicated to my family; past, present and future.

# Certificate of Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Jonathan A. Edgar

10/10/2011

# Acknowledgements

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# Abstract

The ability to synthesise metal nanoparticles with various geometries has vastly improved in recent years. The plasmon resonance, the mechanism responsible for the optical response of metal nanoparticles, is highly sensitive to their geometry. This is the primary reason for the current interest in developing syntheses that produce a distinct geometry. In contrast, polydisperse samples of nanoparticles have relatively poorly defined plasmon resonances. Although nanospheres are still the most common geometry of metal nanoparticle synthesised, there is rapidly increasing interest in nanorods and nanoshells on account of their more flexible optical response. Therefore, developing a reliable synthesis for nanorods and nanoshells has been a target of much recent research. Gold is the most popular metal for the synthesis of plasmonically active nanoparticles.

In this thesis I present a development of synthesis methods for plasmonically active nanoparticles and a characterisation of the resulting products. In my work I have synthesised gold nanorods, a mixed dispersion of gold nanorings and hollow gold nanoparticles, silver nanorods and platinum nanospheres. To characterise these nanoparticles I have used a range of techniques including UV-Vis-NIR spectrometry, SEM, TEM, cryo-TEM, SAXS and electrodynamics simulations.

Early in my work I recognised that gold nanorods provided the best opportunities to achieve large scale applications. Some significant drawbacks in the existing methods of synthesis were identified, such as the inefficient reaction of gold. This realisation led me to focus the majority of my efforts on improving the understanding of the mechanisms involved in the synthesis of gold nanorods and, in particular, on the all-important transition from spherical seed particle to anisotropic rod. The nearest competitor to nanorods, with respect to applications, is nanoshells and so I have also compared these two geometries in the literature review.

From the exhaustive work presented in this thesis I present a set of optimum conditions for the synthesis of gold nanorods. Evidence for the disproportionation of gold (I) bromide as the mechanism of gold metal formation in the gold nanorod synthesis is presented. I also show that it is necessary to sacrifice control of the aspect ratio of the nanorods produced in order to improve the efficiency of the reaction. I use a co-reductant to show that the formation of nanorods is dependent on the effectiveness of the reductant that is present after the addition of the gold nanoparticle seeds. It is also apparent that it is possible to achieve a range of aspect ratios as well as particle dimensions by varying the amount of seed particles added to the growth solution.

I have used a range of experimental techniques including cryo-TEM, SEM, UV-Vis spectroscopy and small angle X-ray scattering to probe the physical dimensions and optical properties of gold nanorods at various stages of their growth and from this I have developed a new growth model. Simulations of the optical properties of the intermediate nanoparticle geometries observed support this new growth model.

# Table of Contents

# List of Publications

Portions of the work presented in this thesis have been published, contributed to or have been submitted for publication. The following is a list of the citations for these publications:

**Jonathan A. Edgar**, Hadi M. Zareie, Martin G. Blaber, Annette Dowd, Michael B. Cortie

"Synthesis of hollow gold nanoparticles and rings using silver templates"

*2008 International Conference on Nanoscience and Nanotechnology* **2008**, 36-39.

**Jonathan A. Edgar**, Michael B. Cortie

"Nanotechnological Applications of Gold Nanoparticles"

*Gold: Science and applications*. CRC Press: **2009**; p 369-397.

Andrey I. Denisyuk, Giorgio Adamo, Kevin F. MacDonald, Nikolay I. Zheludev, Matthew D. Arnold, **Jonathan A. Edgar**, Michael J. Ford, Viktor Myroshnychenko, Javier García de Abajo

"Transmitting hertzian optical nanoantenna with free-electron feed"

*Nano Letters* **2010,** 10, (9), 3250 – 3252

Nicholas L. Stokes, **Jonathan A. Edgar**, Andrew M. McDonagh, Michael B. Cortie

"Spectrally selective coatings of gold nanorods on architectural glass"

*Journal of Nanoparticle Research* **2010,** 12, (8), 2821 - 2830

**Jonathan A. Edgar**, Andrew M. McDonagh, Michael B. Cortie

"On the mechanism of formation of gold nanorods"

ACS Nano **2011** submitted

# List of Abbreviations

| | |
|---|---|
| $^{1}$H-NMR | nuclear magnetic resonance spectroscopy |
| A* | ascorbate radical |
| Ag or $Ag^{o}$ | silver metal |
| $Ag^{+}$ | silver ion |
| AgBr | silver bromide |
| $AgNO_3$ | silver nitrate |
| AMMRF | Australian microscopy and microanalysis research facility |
| AR | aspect ratio |
| Au or $Au^{o}$ | gold metal |
| $Au_2S$ | gold sulphide |
| $Au^{3+}$ | gold (III) ion |
| $AuBr_2^-$ | gold (I) bromide |
| $AuBr_4^-$ | gold (III) bromide |
| $AuCl_2^-$ | gold (I) chloride |
| $AuCl_4^-$ | gold (III) chloride |
| BDAC | hexadecyl-benzyldimethyl-ammonium chloride |
| $BH_4^-$ | borohydride |
| $Br^-$ | bromide |
| BSA | bovine serum albumin |
| BT | bow-tie |
| $C_{16}$TABr | hexadecyltrimethylammonium bromide |
| $C_{16}$TACl | hexadecyltrimethylammonium chloride |
| $C_{16}$TASBr | AgBr- $C_{16}$TABr complex |
| $C_{16}$TEABr | hexadecyl-triethylammonium bromide |
| CBT | conically-capped bow-tie |
| CC | conically-capped cylinder |
| CCG | complex conjugate gradient |
| CdSe-ZnS | cadmium selenide - zinc sulphide |
| CM | Clausius-Mossotti |
| CMC | critical micelle concentration |
| cryo-TEM | cryogenic transmission electron microscopy |
| DDA | discrete dipole approximation |
| DHA | dehydro-ascorbic acid |
| DNA | deoxyribonucleic acid |
| EM | electromagnetic |
| et alii | and others' |
| EXAFS | extended X-ray absorption fine structure |
| fastSPS | fast single-particle spectroscopy |
| FCC | face centred cubic |
| FE-SEM | field emission - scanning electron microscope |
| FFT | fast Fourier transform |
| FOM | figure of merit |
| FTIR | Fourier transform infrared spectroscopy |

| | |
|---|---|
| GM | Göppert-Mayer units |
| GS | growth solution |
| $H_2A$ | ascorbic acid |
| $H_2PtCl_6$ | hexachloroplatinic acid |
| $HA^-$ | ascorbate anion |
| $HAuBr_4$ | tetrabromoauric acid |
| $HAuCl_4$ | tetrachloroauric acid |
| HCl | hydrochloric acid |
| HDT | hexadecanethiol |
| $HNO_3$ | nitric acid |
| ICP-MS | inductively coupled plasma - mass spectrometry |
| IR | infrared |
| ITO | indium tin oxide |
| $KBH_4$ | potassium borohydride |
| LDR | lattice dispersion relation |
| LSP | localised surface plasmon |
| MRI | magnetic resonance imaging |
| $Na_2S$ | sodium sulphide |
| NaBr | sodium bromide |
| NaOH | sodium hydroxide |
| NaSal | sodium salicylate |
| NiPAAm | N-isopropylacrylamide |
| NIR | near infrared |
| NP | nanoparticle |
| OCT | optical coherence tomography |
| OH | hydroxide |
| PC | personal computer |
| PTFE | polytetrafluoroethylene |
| PVA | poly-vinyl alcohol |
| PVP | polyvinylpyrrolidone |
| QDs | quantum dots |
| RIU | refractive index unit |
| rpm | revolutions per minute |
| SALDI-MS | surface-assisted laser desorption/ionisation time-of-flight mass spectrometry |
| SAXS | small angle X-ray scattering |
| SC | spherically-capped cylinder |
| SEM | scanning electron microscopy |
| SERS | surface enhanced Raman scattering |
| SHE | standard hydrogen electrode |
| $SiO_2$ | silicon dioxide |
| SPIO | super-paramagnetic iron oxide |
| SPP | surface plasmon polariton |
| $TC_{12}ABr$ | tetradodecylammonium bromide |

| | |
|---|---|
| $TC_8ABr$ | tetraoctylammonium bromide |
| TEM | transmission electron microscopy |
| TGA | thermogravimetric analysis |
| TPL | two-photon induced luminescence |
| UPD | underpotential deposition |
| UV | ultraviolet |
| Vis | visible |
| WAXS | wide angle X-ray scattering |
| XPS | X-ray photoelectron spectroscopy |

# List of Figures